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(54) Title: MANUFACTURE OF CELLULOSIC ARTICLES

(57) Abstract

An aqueous solution of an alkali metal hydroxide, preferably sodium hydroxide, containing from 0.2 to 3.85 percent by weight hydroxide ions is applied to a never-dried cellulosic article, for example fibre or film, being produced by the lyocell process. The method of the invention confers increased dyability on the cellulosic article, and it may also confer increased absorbency, increased whiteness and/or reduced yellowness thereon.

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MANUFACTURE OF CELLULOSIC ARTICLES

Technical field

This invention relates to methods of manufacturing extruded lyocell articles, including fibres and films, with particular reference to increasing the dyeability of such articles and to improving their properties in certain other ways.

Background art

It is known that cellulose fibre can be made by extrusion of a solution of cellulose in a suitable solvent into a coagulating bath. This process is referred to as "solvent-spinning", and the cellulose fibre produced thereby is referred to as "solvent-spun" cellulose fibre or as lyocell fibre. Lyocell fibre is to be distinguished from cellulose fibre made by other known processes, which rely on the formation of a soluble chemical derivative of cellulose and its subsequent decomposition with the regeneration of cellulose, for example the viscose process. Lyocell fibres are known for their impressive textile-physical properties such as tenacity in comparison with fibres such as viscose rayon fibres. One example of a solvent-spinning process is described in US-A-4,246,221, the contents of which are incorporated herein by way of reference. Cellulose is dissolved in a solvent such as an aqueous tertiary amine N-oxide, for example N-methylmorpholine N-oxide. The resulting solution is then extruded through a die into an aqueous bath to produce an assembly of filaments, which is washed with water to remove the solvent and is subsequently dried. Lyocell films can be manufactured by analogous procedures.

Lyocell can be dyed with conventional dyestuffs for cellulose. There is a desire for extruded lyocell articles which exhibit increased dyeability. In particular, there is a desire for lyocell fibres which exhibit similar dyeing characteristics to those of cotton. It is one object of the invention to provide a simple method of manufacturing such

articles. Further objects of the invention, which may be achieved under defined conditions, include the manufacture of lyocell articles having increased whiteness, reduced yellowness and/or increased absorbency.

Disclosure of invention

According to the present invention there is provided a method for the manufacture of an extruded lyocell article, including the steps in sequential order of:

(1) extruding a solution of cellulose in an organic solvent through a die, thereby producing an elongate form;

(2) passing the elongate form through at least one water-containing bath to remove the organic solvent therefrom, thereby producing a never-dried reconstituted cellulosic member;

(3) as characterising step, applying to the never-dried reconstituted cellulosic member an aqueous solution of an alkali metal hydroxide, the solution containing 0.20 to 3.85 percent by weight hydroxide ions;

(4) washing the reconstituted cellulosic member to remove alkali metal hydroxide therefrom; and

(5) drying the reconstituted cellulosic member, thereby forming the extruded lyocell article.

The alkali metal hydroxide is preferably sodium hydroxide. The concentration of sodium hydroxide in the solution applied to the fibre is often in the range 0.5 to 9 percent by weight. On the one hand, it has generally been found that treatment with solutions of lower concentration does not confer as great an increase in dyeability as may be desired. On the other hand, it has generally been found that treatment with solutions of higher concentration may result in excessive swelling of the reconstituted cellulosic member and dissolution of lower molecular weight cellulose fractions therefrom into the alkali metal hydroxide solution. In comparison with conventional lyocell articles,

the method of the invention may advantageously be found to provide increased whiteness, decreased yellowness and increased lustre. It has surprisingly and advantageously been found that lyocell articles produced by the method of the invention may be of higher whiteness and lower yellowness than lyocell articles bleached in conventional manner with a bleaching agent such as sodium hypochlorite or hydrogen peroxide. Use of sodium hydroxide solutions having a concentration in the range 0.5 to 2 percent by weight may advantageously be found to permit the production of lyocell articles having increased tenacity, increased dyeability, increased water imbibition and increased absorbency when made into absorbent articles such as tampons. Use of sodium hydroxide solutions having a concentration in the range 3 to 5 percent by weight may advantageously be found to permit the manufacture of lyocell articles having reduced tenacity (although not unacceptably so), markedly increased dyeability, similar or slightly increased water imbibition, and markedly increased absorbency when made into absorbent articles such as tampons. Use of sodium hydroxide solutions having a concentration in the range from 7 to 9 percent by weight may be found to yield extruded lyocell articles, especially fibres, which fibrillate with the formation of fibrils of relatively large diameter when subjected to mechanical working in the wet state and which accordingly may be found useful in papermaking and allied fields.

The alkali metal hydroxide solution may if desired contain a surface-active wetting agent.

The alkali metal hydroxide solution may conveniently be applied to the reconstituted cellulosic member from a circulating bath, although it will be appreciated that other application methods such as padding or spraying may alternatively be employed. In application by means of a circulating bath, the residence time of the reconstituted cellulosic member in the bath may conveniently be in the range 20 to 90 seconds. The solution of alkali metal

hydroxide may conveniently be applied to the reconstituted cellulosic member at reduced, ambient or elevated temperatures, for example in the range from 0 to 60°C, often from 25 to 60°C.

Application of alkali metal hydroxide may be found to plasticise the reconstituted cellulosic member. Care should be taken to avoid undesirable deformation of the member whilst it is in a plasticised state.

It has been found generally advantageous to heat the never-dried reconstituted cellulosic member to which the alkali metal hydroxide has been applied in order to achieve the greatest increase in dyeability and the greatest reduction in differential dyeing, the heating being carried out before the washing step (4). Heating may conveniently be effected by steaming, for example at 100 to 120°C for 1 to 30 minutes. Steaming times in the range 2 to 15 minutes can conveniently be achieved by use of a J-box. Other heating methods such as exposure to RF (radio-frequency) or microwave radiation may alternatively be employed.

The washing step (4) is carried out using water or other aqueous liquor. The washing step (4) may include washing with dilute aqueous acid to ensure that the extruded lyocell article is of neutral or slightly acid pH, for example a pH in the range from 4.5 to 7.

The extrusion and reconstitution steps (1) and (2) and the drying step (5) may be carried out in conventional manner. The organic solvent is preferably an aqueous tertiary amine N-oxide, more preferably aqueous N-methylmorpholine N-oxide.

The alkali metal hydroxide treatment step of the invention is performed on a freshly-extruded lyocell article which has never been dried. It has been found that alkali metal hydroxide treatment of never-dried lyocell is in

general more effective in increasing dyeability than is alkali metal hydroxide treatment of lyocell which has previously been dried.

Relative dyeability can be assessed quantitatively by Q-value techniques. Q-value is defined as the relative depth of colour of a sample against a standard whose depth of colour is assigned the value 100. The depth of colour of a surface can be expressed as the integral of K/S over the range 400 to 700 nm, where K is the absorption coefficient and S is the scattering coefficient. K/S can be calculated from the reflectance value of a surface at a particular wavelength. The integral of K/S is proportionally related to the amount of dye in a sample. In general, a difference in Q-value of 5% or greater will be visibly different to the naked eye. In the context of a method designed to increase dyeability, an increase in Q-value of 10% or greater can be considered to be technically and commercially significant. If an extruded lyocell article which has not been subjected to the alkali metal hydroxide treatment step of the invention is taken as standard and assigned the Q-value 100, the method of the invention can be used to manufacture extruded lyocell articles which exhibit Q-values of 110 or more, often 120 or more. Under suitable conditions, the method of the invention can be used to manufacture extruded lyocell articles which exhibit Q-values up to 140, sometimes up to 150.

Dyed yarns and fibres containing both standard lyocell fibre and lyocell fibre treated by the method of the invention may exhibit an attractive stippled appearance.

The method of the invention is applicable to the manufacture of extruded lyocell articles such as fibres, which may be in the form of staple fibre, tow or continuous filament yarn, and films, which may be in flat or tubular form.

Test Method 1 - Modified Syngina Test

The absorbency of cellulose fibres may be assessed by the following procedure, called the Modified Syngina Test. A well-blended sample of fibre weighing at least 30 g is opened or carded by hand and formed into a web using a Shirley miniature card. The carded web is stored in a conditioned atmosphere (20±2°C, 65±2% relative humidity, RH) for 24 hours. The web is folded lengthways into three layers and cut to form a 100 mm x 45 mm pad weighing 2.72±0.50 g, in which the fibres run parallel to the long dimension of the rectangle. The pad is placed into a cross-die assembly and pressed at 7 x 10^6 Pa (1000 psi) for 60 seconds to form a longitudinally-expanding tampon of nominal length 20 mm and nominal diameter 15 mm having an average density of about 0.35 g/cm^3. The tampon is then stored in a conditioned atmosphere for 2 hours and its length measured. Tampons which have expanded to a length of more than 50 mm during storage are rejected, and if necessary the pressing conditions are adjusted to provide tampons with greater stability to expansion. Tampon absorbency is assessed using the test defined in GB-B-2,094,637, except that 180 mm hydrostatic head water pressure is employed, the Syngina chamber is tilted at 30° to the vertical, and the 1% saline solution is injected into the head of the tampon, using a hypodermic needle, at a rate of 50 ml/hour. Three tampons are tested and the results, reported as grams of saline solution absorbed per gram of fibre (g/g), are averaged. Tampons made from a standard control sample of viscose rayon fibre should be tested in each series of experiments to ensure reproducibility.

Test Method 2 - Q-value Test

The sample of fibre or fabric to be tested (6 g) is placed in a lidded dyeing tube together with dye (Direct Green 27) (0.12 g, 100% basis), sodium chloride (2.4 g) and water (240 ml). The tube is clamped to a rotating spindle in

a water bath at 50°C and the temperature raised to 98°C over 30 minutes. Dyeing is continued at this temperature for 45 minutes. The apparatus is then cooled to 50°C, and the sample is removed, washed and dried.

The colour of the dyed fibre is assessed by reflectance spectrometry using a xenon flash at 20 nm intervals over the range 400 to 700 nm, and K/S at each wavelength is calculated using the formula:

$$K/S = (1-r)^2 / 2r$$

where r = reflectance. The values of K/S are integrated over all the measurements to give a value representing the total colouration of the sample. The Q-value of a sample under test is reported as the ratio of its integrated K/S value to that of a control sample (given the arbitrary Q-value 100).

The method of the invention is illustrated by the following Examples, in which parts and proprortions are by weight unless otherwise specified:-

Example 1

A spinning dope comprising cellulose (15%), N-methylmorpholine N-oxide (NMMO) (75%) and water (10%) was and across through a die (18,000 holes of diameter 70 micron) through an air-gap (30 mm) into an aqueous bath (ambient temperature). The resulting filaments were washed with water until substantially free of NMMO, treated with sodium hydroxide under various conditions, steamed in a steam tunnel at 100-120°C for 1-2 minutes, washed until free of alkali and dried. A control sample was prepared in similar manner except that the treatment with sodium hydroxide was omitted. Further experimental details and results are presented in Table 1:

Table 1

NaOH %	°C	D.P.	dtex	Tenacity cN/tex	Extension %	Q-value	Absorbency g/g
-	-	555	1.58	38.3	13.6	100	3.50
0.5	25	535	1.59	35.5	12.2	106	3.71
1.0	25	491	1.43	40.7	13.0	110	3.87
2.0	50	532	1.39	43.3	13.9	116	3.84
5.0	50	419	1.61	34.0	12.6	141	4.10

Degree of polymerisation (D.P.) was assessed by standard viscosimetric techniques. Q-value was assessed by Test Method 2. Absorbency was measured by the Modified Syngina Test.

Example 2

Example 1 was repeated, except that in some cases steaming was omitted. Experimental details and results are given in Table 2:

Table 2

NaOH %	°C	Steam	D.P.	dtex	Tenacity cN/tex	Extension %	Q-value	Absorbency g/g
-	-	Yes	540	1.56	37.9	13.1	103	4.10
2.0	50	No	543	1.59	38.7	13.5	110	3.66
2.0	50	Yes	465	1.49	37.0	11.7	112	4.09
5.0	50	Yes	525	1.37	41.0	13.8	120	4.08

Example 3

Example 1 was repeated. Sodium hydroxide was applied from a circulating bath at ambient temperature; the concentration of the bath was measured at the beginning

and end of each run. Experimental details and results are given in Table 3.

Table 3

NaOH %		Steaming	Q-value		Absorbency	Whiteness	Yellowness
Beginning	End	min.	Beginning	End	g/g		
-	-	-	100	100	3.52	63.0	4.21
2.67	2.05	-	96	102	3.47	64.3	4.48
2.05	1.50	2	106	108	3.75	67.8	4.00
3.01	2.29	5	109	126	4.24	66.3	3.76
4.60	3.66	2	104	110	3.77	71.2	2.85
4.98	3.90	5	129	126	3.85	68.7	3.52
6.44	5.32	2	118	111	4.02	68.7	3.52
6.40	5.14	5	126	151	3.93	68.4	3.46
9.00	7.68	2	130	128	3.80	70.2	3.53

Bath residence time was 29 seconds when steaming time was 0 or 2 minutes, and it was 63 seconds when steaming time was 5 minutes. Travel time between the bath and the steam tunnel was 21 and 44 seconds, respectively.

Problems were experienced of fibre sticking to process rolls at the highest NaOH concentration. Water imbibition of the treated samples ranged from 53 to 59% (control 54%).

The Syngina absorbencies of the control sample and of the sample prepared with starting NaOH concentration 3.01% were assessed using lyocell fibre which had been crimped by the process described in WO-A-94/28220 and US Patent Application Serial No. 08/428,424 the contents of which are incorporated herein by way of reference. It is well-known that in general crimped fibre lends itself to the production of articles of higher absorbency than does uncrimped fibre. This should be taken into account when comparing the absorbency of the uncrimped fibre samples with that of the control.

Whiteness and yellowness were measured according to the CIELab 1976 system using an ICS-Texicon Spectraflash 500 (Trade Mark) spectrophotometer illuminated by a pulsed xenon flash lamp, the flash being filtered through a D65 filter to simulate daylight. Light reflected from a sample of fibre is passed through a diffraction grating, and the intensity of the radiation at different wavelengths is assessed. The spectrophotometer software compares the intensity of this radiation with that emitted by the light source and reports the whiteness and yellowness (B) values of the sample. Higher whiteness values represent whiter fibres, and lower yellowness values represent less yellow fibres. Both are accordingly to be preferred.

CLAIMS

1. A method for the manufacture of an extruded lyocell article, including the steps in sequential order of:

(1) extruding a solution of cellulose in an organic solvent through a die, thereby producing an elongate form;

(2) passing the elongate form through at least one water-containing bath to remove the organic solvent therefrom, thereby producing a never-dried reconstituted cellulosic member;

(3) as characterising step, applying to the never-dried reconstituted cellulosic member an aqueous solution of an alkali metal hydroxide, the solution containing 0.2 to 3.85 percent by weight hydroxide ions;

(4) washing the reconstituted cellulosic member to remove alkali metal hydroxide therefrom; and

(5) drying the reconstituted cellulosic member, thereby forming the extruded lyocell article.

2. A method according to claim 1, characterised in that the alkali metal hydroxide is sodium hydroxide.

3. A method according to either one of the preceding claims, characterised in that the temperature of the aqueous solution of alkali metal hydroxide applied to the reconstituted cellulosic member is in the range from 0 to 60°C.

4. A method according to claim 3, characterised in that the temperature of the aqueous solution of alkali metal hydroxide applied to the reconstituted cellulosic member is in the range from 25 to 60°C.

5. A method according to any one of the preceding claims, characterised in that the aqueous solution of

alkali metal hydroxide additionally comprises a surface-active wetting agent.

6. A method according to any one of the preceding claims, characterised in that it additionally includes between steps (3) and (4) the step (3a) of steaming the never-dried reconstituted cellulosic member to which the aqueous solution of alkali metal hydroxide has been applied.

7. A method according to claim 6, characterised in that the steaming step (3a) is conducted at a temperature in the range from 100 to 120°C for a time in the range from 1 to 30 minutes.

8. A method according to any one of the preceding claims, characterised in that the washing step (4) includes an aqueous acidic wash whereby the pH of the extruded lyocell article is neutral or slightly acidic.

9. A method according to any one of the preceding claims, characterised in that the organic solvent is aqueous N-methylmorpholine N-oxide.

10. A method according to any one of the preceding claims, characterised in that the extruded lyocell article takes the form of fibre or film.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D01F2/00 C08J5/18 //C08L1:02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 24524 A (COURTAULDS FIBRES HOLDINGS LTD ;TAYLOR JAMES MARTIN (GB)) 14 September 1995 see the whole document ---	1-10
A	WO 95 28516 A (COURTAULDS FIBRES HOLDINGS LTD ;POTTER CHRISTOPHER DAVID (GB); DOB) 26 October 1995 see the whole document ---	1-10
A	WO 92 14871 A (COURTAULDS PLC) 3 September 1992 see the whole document -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No
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